

APPENDIX
A CLEAN VERSION OF EACH REPLACEMENT PARAGRAPHS
OF THE SPECIFICATION

Clean version of page 1 first paragraph:

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U.S. Serial

No. 09/279,498 Filed 03/28/99

~~No. 33, Entitled: "Tear Resistant Elastic Crystal Gels, Gel Composites, and Their Uses", filed March 23, 1999;~~ Serial Nos: 08/130,545, filed August 8, 1998; 08/984,459, filed 12/3/97; 08/909,487, filed 7/12/97; 08/863,794, filed 5/27/97; 08/819,675 filed March 17, 1997, now U. S. Patent No. 5,884,639; PCT/US97/17534, filed 30 September 1997; U.S. Serial No: 08/719,817 filed September 30, 1996, U.S. Serial No: 08/665,343 filed June 17, 1996 which is a Continuation-in-part of U.S. Serial No: 08/612,586 filed March 8, 1996; PCT/US94/04278 filed 4/19/94 (published 5/26/95 No. WO95/13851); PCT/US94/07314 filed 6/27/94, 08/ (published 1/4/96 No. WO 96/00118); 08/288,690 filed 8/11/94; 08/581,188 filed 12/29/95; 08/581,191 filed 12/29/95; 08/581,125 filed 12/29/95. In turn U.S. Serial Nos: 08/581,188; 08/581,191; and 08/581,125 are continuation-in-parts of the following applications: Serial Nos.: 08/288,690, filed August 11, 1994, PCT/US94/07314 filed June 27, 1994 (CIP of PCT/US 94/04278, filed 19 April 1994). The above patents and applications are specifically incorporated herein by reference.

Clean version of page 2 second and 3rd paragraphs:

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I have discovered novel non-tacky, optically "water" clear crystalline gels which do not require surface activation by additives, hereafter referred to as simply "crystal N-gels" or more simply "N-gels". The crystal N-gels of the invention are made from: (1) one or more thermoplastic elastomer copolymers and block copolymers having a selective amounts of one or more substantially crystalline polyethylene components and which copolymers having a selected amount of one or more glassy components or combined to form a mixture with (2) a selective amounts of one or more glassy homopolymers, and (3) a selective plasticizers. The combination of (1)-(3) provides for optically clear, non-tacky properties that is uniform throughout the N-gels' volume. The crystal N-gels advantageously exhibit higher tear

resistance and rupture resistance than amorphous copolymer gels of corresponding rigidities which lacks substantially crystalline polyethylene components. The non-tacky and optical properties of the crystal N-gels do not rely on powders or surface activation by additives to establish their non-tackiness. The crystal N-gels' non-tackiness pervasive the gels' entire volume. No matter how deep or in which direction a cut is made, the gels are non-tacky throughout (at all points internally as well as on the gels' surface). Once the N-gel is cut, the crystal N-gels of the invention immediately exhibits non-tackiness at its newly cut surface. Hence, the homogeneity of the non-tackiness and optical properties of the crystal N-gels of the invention are not found in any other prior art gels.

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The crystal N-gels of the invention more particularly comprises: (1) 100 parts by weight of one or more copolymers having one or more glassy components and one or more elastomeric (non-glassy) components, wherein said elastomeric components comprises one or more substantially crystalline polyethylene components, said copolymers are of the general types: (i) linear triblock copolymers, (ii) multi-arm block copolymers, (iii) branched block copolymers, (iv) radial block copolymers, (v) multiblock copolymers, and (vi) Interpolymers produced by metallocene catalysts, using single site, constrained geometry addition polymerization catalysts; said copolymers are characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 25°C as determined by DSC curve; said glassy components selected from polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstryene), and poly(p-methylstyrene), wherein the amounts of glassy to non-glassy components of said copolymers forming said gels having a ratio (a) of at least 37:63 with the proviso that in the event said

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ratio (a) being less than 37:63, a selective amounts of (2) one or more glassy homopolymers selected from polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstryene), poly(p-methylstyrene) and poly(dimethylphenylene oxide) are added to form a mixture of said copolymers and said glassy homopolymers wherein said amounts of glassy components of said copolymers and said glassy homopolymers to said non-glassy components of said copolymers forming said gels having a ratio (b) of at least 37:63, wherein

said glassy homopolymers having typically an average molecular weight ranging from about 2,500 to about 90,000; and (3) selected amounts of one or more compatible plasticizers sufficient to achieve gel rigidities of from less than about 2 gram Bloom to about 2,000 gram Bloom, wherein said plasticizers having a viscosity cSt @ 40°C off at least not greater than about 30. Additionally said crystal N-gels can be formed with or without a major or minor amounts of one or more other (vii) copolymers or polymers described below.

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The crystal N-gels of the invention are also suitable in physically interlocking or forming with other selected materials to form composites combinations. The materials are selected from the group consisting of paper, foam, plastic, fabric, metal, metal foil, concrete, wood, glass, various natural and synthetic fibers, including glass fibers, ceramics, synthetic resin, and refractory materials.

As use herein, the term "tack level" in gram-Tack is determined by the gram weight displacement force to lift a polystyrene reference surface by the tip of a 16 mm diameter hemi-spherical gel probe in contact with said reference surface as measured on a scale at 23°C.

As used herein, the term "gel rigidity" in gram Bloom is determined by the gram weight required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square centimeter at 23°C.

Amend page 3, under Description of the Drawings:

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Figs 1. Illustrates G_n and M_n of the composites of the invention.

Figs 2a - 2d. Representative crossections of G_n and M_n combinations of the composites of the invention.

Figs 3a - 3n. Representative crossection of G_n and M_n combination of the composites of the invention.

Figs 4a-4w. Representative crossection of G_n and M_n combination of the composites of the invention.

Figs. 5a. Representative crossection of face mask construction.

Fig. 5b. Representative side view of face mask.

Clean version of page 4, 1st paragraph combine with last sentence:

Meeting, Wiesbaden, 1983; Kautsch, Gummi, Kunstst. 37, 284 (1984). (2) W.P. Gergen, et al., "Hydrogenated Block Copolymers," Paper No. 57, presented at a meeting of the Rubber Division ACS, Los Angeles, April 25, 1985. Encyclopedia of Polymer Science and Engineering, Vol. 2, pp 324-434, "Block Copolymers". (3) L. Zotteri and et al., "Effect of hydrogenation on the elastic properties of poly(styrene-b-diene-b-styrene) copolymers", Polymer, 1978, Vol. 19, April. (4) J. Kenneth Craver, et al., Applied Polymer Science, Ch. 29, "Chemistry and Technology of Block Polymers", pp. 394-429, 1975. (5) Y. Mahajer and et al., "The influence of Molecular Geometry on the Mechanical Properties of homopolymers and Block Polymers of Hydrogenated Butadiene and Isoprene" reported under U.S. ARO Grant No. DAAG29-78-G-0201. (6) J. E. McGrath, et al., "Linear and Star Branched Butadiene-Isoprene Block Copolymers and Their Hydrogenated Derivatives", Chem. Dept, Virginia Polytechnic Institute and State University Blacksburg, VA, reported work supported by Army Research Office. (7) Legge, Norman R., "Thermoplastic Elastomers", Charles Goodyear Medal address given at the 131st Meeting of the Rubber Division, American Chemical Society, Montreal, Quebec, Canada, Vol. 60, G79-G115, May 26-29, 1987. (8) Falk, John Carl, and et al., "Synthesis and Properties of Ethylene-Butylene-1 Block Copolymers", Macromolecules, Vol. 4, No. 2, pp. 152-154, March-April 1971. (9) Morton, Maurice, and et al., "Elastomeric Polydiene ABA Triblock Copolymers within Crystalline End Blocks", University of Arkon, work supported by Grant No. DMR78-09024 from the National Science Foundation and Shell Development Co. (10) Yee, A. F., and et al., "Modification of PS by S-EB-S Block Copolymers: Effect of Block Length", General Electric Corporate Research & Development, Schenectady, NY 12301. (11) Siegfried, D. L., and et al., "Thermoplastic Interpenetrating Polymer Networks of a Triblock Copolymer elastomer and an Ionomeric Plastic Mechanical Behavior", Polymer Engineering and Science, Jan. 1981, Vol. 21, No.1, pp 39-46. (12) Clair, D. J., "S-EB-S Copolymers Exhibit Improved Wax Compatibility", Adhesives Age, November, 1988. (13) Shell Chemical Technical Bulletin SC:1102-89, "Kraton® Thermoplastic Rubbers in oil gels", April 1989. (14) Chung P. Park and George P. Clingerman, "Compatibilization of Polyethylene-Polystyrene Blends with Ethylene-Styrene

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Random Copolymers", the Dow Chemical Company, May 1996. (15) Steve Hoenig, Bob Turley and Bill Van Volkenburgh, "Material Properties and Applications of Ethylene-Styrene Interpolymers", the Dow Chemical Company, September 1996. (16) Y. Wilson Cheung and Martin J. Guest, "Structure, Thermal Transitions and Mechanical Properties of Ethylene/Styrene Copolymers", the Dow Chemical Company, May 1996. (17) Teresa Plumley Karjaia, Y. Wilson Cheung and Martin J. Guest, "Melt Rheology and Processability of Ethylene/Styrene Interpolymers", the Dow Chemical Company, May 1997. (18) D. C. Prevorsek, et al., "Origins of Damage Tolerance in Ultrastrong Polyethylene Fibers and Composites", Journal of Polymer Science: Polymer Symposia No. 75, 81-104 (1993). The above applications, patents and publications are specifically incorporated herein by reference.

Clean version of page 5:

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copolymers involving the addition of solvating agents such as ethers just before the final styrene charge is added, any excess of ethers can alter the polybutadiene structure from a 1,4-cis or trans structure to a 1,2- or 3,4-addition polymer. Using difunctional coupling agent would give linear block copolymers and multifunctional agents would give star-shaped or radial block copolymers. Hydrogenation of the 1,4-polybutadiene structure yields polyethylene, while that of the 1,2-polybutadiene yields polybutylene. The resulting polyethylene will be essentially identical with linear, high-density polyethylene with a melting point, T_m , of about 136°C . Hydrogenation of 1,2-polybutadiene would yield atactic poly(1-butene) (polybutylene). The T_g of polybutylene is around -18°C . Random mixtures of ethylene and butylene units in the chain would suppress crystallinity arising from polyethylene sequences. The objective for a good elastomer should be to obtain a saturated olefin elastomeric segment with the lowest possible T_g and the best elastomeric properties. Such an elastomer favored using styrene as the hard-block monomer and selecting the best monomer for hydrogenation of the elastomer midsegment. Using a mixture of 1,4- and 1,2-polybutadiene as the base polymer for the midsegment would result in an ethylene/butylene midsegment in the final product. The elements of selection of the midsegment composition is elastomer crystallinity and the elastomer T_g of an ethylene/butylene copolymer. Very low

levels of crystallinity can be achieved around 40-50% butylene concentration. The minimum in dynamic hysteresis around 35% butylene concentration in the elastomeric copolymer. A value of 40% butylene concentration in the ethylene/butylene midsegment was chosen for the S-EB-S block copolymers.

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Clair's paper teaches that the EB midblock of conventional S-EB-S polymers is a random copolymer of ethylene and 1-butene exhibiting nearly no crystallinity in the midblock. In the preparation of ethylene-butylene (EB) copolymers, the relative proportions of ethylene and butylene in the EB copolymer chain can be controlled over a broad range from almost all ethylene to almost all butylene. When the EB copolymer is nearly all ethylene, the methylene sequences will crystallize exhibiting properties similar to low density polyethylene. In differential scanning calorimeter (DSC) curves, the melting endotherm is seen on heating and a sharp crystallization exotherm is seen on cooling. As the amount of butylene in the EB copolymer is increased, the methylene sequences are interrupted by the ethyl side chains which shorten the methylene sequences length so as to reduce the amount of crystallinity in the EB copolymer. In conventional S-EB-S polymers, the amount of 1-butene is controlled at a high enough level to make the EB copolymer midblock almost totally amorphous so as to make the copolymer rubbery and soluble in hydrocarbon solvents. Clair suggests that an S-EB-S polymer retaining at least some crystallinity in the EB copolymer midblock may be desirable. Therefore, a new family of S-EB-S polymers are developed (U.S. Patent No. 3,772,234) in which the midblock contains a higher percentage of ethylene. The molecular weights of the new crystalline midblock segment S-EB-S polymers can vary from low molecular weight, intermediate molecular, to high molecular weight; these are designated Shell GR-3, GR-1, and GR-2 respectively. Unexpectedly, the highest molecular weight polymer, GR-2 exhibits an anomalously low softening point. A broad melting endotherm is seen in the DSC curves of these polymers. The maximum in this broad endotherm occurs at about 40°C.

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Himes, et al., (4,880,878) describes SEBS blends with improved resistance to oil absorption.

Papers (14) - (17) describes poly(ethylene-styrene) random copolymers (Dow Interpolymers™): Dow S, M and E Series produced by metallocene catalysts, using single

site, constrained geometry addition polymerization catalysts resulting in poly(ethylene-styrene) random copolymers with weight average molecular weight (M_w) typically in the range of 1×10^5 to 4×10^5 , and molecular weight distributions (M_w/M_n) in the range of 2 to 3.

Prevorsek, et al., using Raman spectroscopy, WAXS, SAXD, and EM analysis interprets damage tolerance of ultrastrong PE fibers attributed to the nano scale composite structure that consists of needle-like- nearly perfect crystals that are covalently bonded to a rubbery matrix with a structure remarkably similar to the structure of NACRE of abalone shells which explains the damage tolerance and impact resistance of PE fibers. PE because of its unique small repeating unit, chain flexibility, ability to undergo solid state transformation of the crystalline phase without breaking primary bonds, and its low glass transition temperature which are responsible for large strain rate effects plays a key role in the damage tolerance and fatigue resistance of structures made of PE fibers.

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In general, the overall physical properties of amorphous gels are better at higher gel rigidities. The amorphous gels, however, can fail catastrophically when cut or notched while under applied forces of high dynamic and static deformations, such as extreme compression, torsion, high tension, high elongation, and the like. Additionally, the development of cracks or crazes resulting from a large number of deformation cycles can induce catastrophic fatigue failure of amorphous gel composites, such as tears and rips between the surfaces of the amorphous gel and substrates or at the interfaces of interlocking material(s) and gel. Consequently, such amorphous gels are inadequate for the most demanding applications involving endurance at high stress and strain levels over an extended period of time.

The various types of copolymers and block copolymers employed in forming the crystal N-gels of the invention are of the general configurations $(Y-AY)_n$ copolymers, A-Z-A, and $(A-Z)_n$ block copolymers, wherein the subscript n is a number of two or greater. In the case of multiarm block copolymers where n is 2, the block copolymer denoted by $(A-Z)_n$ is A-Z-A. It is understood that the coupling agent is ignored for sake of simplicity in the description of the $(A-Z)_n$ block copolymers.

The segment (A) comprises a glassy amorphous polymer end block segment which can be polystyrene, poly(alpha-methylstyrene), poly(o-methylstyrene), poly(m-methylstyrene),

poly(p-methylstyrene) and the like, preferably, polystyrene.

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The segment (Y) of copolymers (Y-AY)_n comprises substantially crystalline poly(ethylene) (simply denoted by "-E-" or (E)). In the case of copolymers (A-Y)_n, (Y) when next to (A) may be substantially non-crystalline or amorphous ethylene segments. For example a crystalline copolymer (Y-AY)_n may be represented by:.... -E-E-E-E-E-E-E-E-E-SE-E-E-E-E-E-E-SE-E-E-E-E-E-E-SE-.... Where Y is a long run of polyethylenes or a non-crystalline copolymer (AY-AY)_n: ...-E-SE-SE-E-SE-E-SE-E-SE-E-E-SE-SE-E-SE-...., Where Y is a non-crystalline run of ethylene.

Clean version of page 7, 2nd, 3rd, 4th, and 5th pagragrphs:

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"The linear block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30oC 30oC of from less than about 40 cps to about 60 cps and higher, advantageously from about 40 cps to about 160 cps and higher, more advantageously from about 50 cps to about 180 cps and higher, still more advantageously from about 70 cps to about 210 cps and higher, and even more advantageously from about 90 cps to about 380 cps and higher.

The branched, star-shaped (radial), or multiarm block copolymers are characterized as having a Brookfield Viscosity value at 5 weight percent solids solution in toluene at 30oC 30oC of from about 80 cps to about 380 cps and higher, advantageously from about 150 cps to about 260 cps and higher, more advantageously from about 200 cps to about 580 cps and higher, and still more advantageously from about 100 cps to about 800 cps and higher.

The poly(ethylene/styrene) copolymers, type S series has more than 50 wt% styrene and is glassy at short times and rubbery at long times and exhibits ambient Tg, melt density of about higher than 0.952 to about 0.929 and less, typical Mw = about less than 150,000 to 350,000 and higher.

The type M series has more than 50 wt% styrene is amorphous rubber and exhibits very low modulus, high elasticity, low Tg of from greater than 10oC 10oC to less than -50oC - 50oC, melt Index of from higher than 5 to less than about 0.1, melt density of higher than 0.93 to 9.0 and less, typical Mw = about less than 200,000 to 300,000 and higher.

The type E series contains up to 50 wt% styrene is semi-crystalline rubber and exhibits

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low Tg of from greater than 0°C to about less than -70, low modulus semi-crystalline, good compression set, Melt Index of from about higher than 2 to less than 0.03, melt density of about higher than 0.90 to 0.805 and less, Mw = about less than 250,000 to 350,000 and higher."

Clean version of page 10, paragraphs (a) and (b):

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(a) the non-tacky gels are made from A-Z-A, (A-Z)_n, (A-Y)_n and (Y-AY)_n copolymers: crystalline block copolymers and crystalline poly(ethylene-styrene) random copolymers of the type S, M, and E series (for example SEEPS, S-E-EB-S, S-EB45-EP-S, S-E-EB25-S, S-E-EP-E-S, S-EP-E-S, S-EP-E-EP-S, E-S-E, (E-S)_n, (E-S-E)_n, and (S-E-EP)_n, crystalline S-EB-S with ethylene to butylene midblock ratios (E:B) of 89:11, 88:12, 87:13, 86:14, 85:15, 84:16, 83:17, 82:18, 81:19, 80:20, 79:21, 78:22, 77:23, 76:24, 75:25, 74:26, 73:27, 72:28, 71:29, and 70:30) and the like;

(b) the non-tacky gels are made from copolymers having crystalline poly(ethylene) segments exhibit melting endotherm values of at least about 25°C, 26°C, 27°C, 28°C, 29°C, 30°C, 31°C, 32°C, 33°C, 34°C, 35°C, 36°C, 37°C, 38°C, 39°C, 40°C, 41°C, 42°C, 43°C, 44°C, 45°C, 46°C, 47°C, 48°C, 49°C, 50°C, 51°C, 52°C, 53°C, 54°C, 55°C, 56°C, 57°C, 58°C, 59°C, 60°C, 61°C, 62°C, 63°C, 64°C, 65°C, 66°C, 67°C, 68°C, 69°C, 70°C, 71°C, 72°C, 73°C, 74°C, 75°C, 76°C, 77°C, 78°C, 79°C, 80°C, and higher; and

Clean version of page 12, 1st paragraph:

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Such an event would demonstrate the tackiness of a gel probe having sufficient tack on the probe surface. The N-gels of the invention fails to lift off the polystyrene reference from the surface of the scale when subject to the foregoing reference tack test. Advantageously, the N-gels of the invention can register a tackiness level of less than 5, more advantageously, less than 3, still more advantageously, less than 2, and still more advantageously less than 1. The non-tackiness of the N-gels of the invention can advantageously range from less than 6 to less than 0.5 grams, typical tack levels are less than 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.5, 2.8, 3.0, 3.5, 4.0, 4.5, 5.0 grams and the like. Whereas probes of gels made from amorphous gels such as SEPS, SEBS, S-EP-EB-S, and the like with copolymer styrene to rubber ratio of less than 37:63 and

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plasticizer of higher than 30 cSt 40°C are found to lift the polystyrene reference from the surface of the scale. For purposes of indicating tack, the method above can provide gel tack level readings of 1, 2, 3, 4, 5, 6, and 7 grams. More accurate and sensitive readings can be made using electronic scales of tack levels of less than 1 gram. By this simple method tack levels (of a gel probe on a polystyrene reference surface) can be measure in terms of gram weight displacement of a scale initially tared to zero. For purpose of the present invention the method of using a polystyrene reference surface having a weight of 7.6 grams in contact and being lifted by the tackiness of a cylindrical gel probe having a 16 mm diameter hemi-spherical tip is used to determine the tackiness of the N-gels of the invention. The level of tack being measured in gram Tack at 23°C.

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copolymer structure becomes cylindrical; and above about 45% A blocks, the structure becomes less cylindrical and more plate like.

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In order to obtain elastic crystal N-gels of the invention, it is necessary that the selective synthesis of butadiene produce sufficient amounts of 1,4 poly(butadiene) that on hydrogenation can exhibit "crystallinity" in the midblocks. In order for the block copolymers forming the crystal N-gels of the invention to exhibit crystallinity, the crystalline midblock segments must contain long runs of -CH₂- groups. There should be approximately at least 16 units of -(CH₂)- in sequence for crystallinity. Only the -(CH₂)₄ units can crystallize, and then only if there are at least 4 units of -(CH₂)₄ in sequence; alternatively, the polyethylene units are denoted b [-(CH₂-CH₂-CH₂-CH₂)-]₄, [-(CH₂)₄]₄ or -(CH₂)₁₆. The amount of -(CH₂)₁₆ units forming the (E) midblocks of the block copolymers comprising the crystal N-gels of the invention should be at least about 20% which amount is capable of exhibiting a melting endotherm in differential scanning calorimeter (DSC) curves.

Advantageously, the elastomer midblock segment should have a crystallinity of at least about 20% of -(CH₂)₁₆ units of the total mole % forming the midblocks of the block copolymer, more advantageously at least about 25%, still more advantageously at least about 30%, especially advantageously at least about 40% and especially more advantageously at least about 50% and higher. Broadly, the crystallinity of the midblocks

should range from at least about 20% to about 60%, less broadly from at least about 18% to about 65%, and still less broadly from at least 22% to about 70%.

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The melting endotherm in DSC curves of the crystalline block copolymers comprising at least 20% crystallinity are much higher than conventional amorphous block copolymers. The poly(ethylene) crystalline segments or midblocks of copolymers forming the crystal N-gels of the invention are characterized by sufficient crystallinity as to exhibit a melting endotherm of at least about 25°C, more advantageously of about 40°C or higher as determined by DSC curve. The maximum in the endotherm curves of the crystalline block copolymers occurs at about 40°C, but can range from greater than about 25°C to about 60°C and higher. The crystalline block copolymers forming the crystal N-gels of the invention can exhibit melting endotherms (as shown by DSC) of about 25°C to about 75°C and higher. More specific melting endotherm values of the crystalline midblock block copolymers include: about 28°C, 29°C, 30°C, 31°C, 32°C, 33°C, 34°C, 35°C, 36°C, 37°C, 38°C, 39°C, 40°C, 41°C, 42°C, 43°C, 44°C, 45°C, 46°C, 47°C, 48°C, 49°C, 50°C, 51°C, 52°C, 53°C, 54°C, 55°C, 56°C, 57°C, 58°C, 59°C, 60°C, 61°C, 62°C, 63°C, 64°C, 65°C, 66°C, 67°C, 68°C, 69°C, 70°C, 71°C, 72°C, 73°C, 74°C, 75°C, 76°C, 77°C, 78°C, 79°C, 80°C, 90°C, 100°C, 110°C, 120°C, and higher, whereas, the melting endotherm (DSC) for conventional amorphous midblock segment block copolymers are about 10°C and lower.

The melting endotherm is seen on heating and a sharp crystallization exotherm is seen on cooling. Such midblock crystallization endothermic and exothermic characteristics are missing from DSC curves of amorphous gels. The crystallization exotherm and fusion endotherm of the crystalline block copolymer gels of the invention are determined by ASTM D 3417 method.

Clean version of page 14, 1st and 2nd paragraphs:

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"Generally, the method of obtaining long runs of crystalline $-(CH_2)-$ is by sequential block copolymer synthesis followed by hydrogenation. The attainment of crystal N-gels of the instant invention is solely due to the selective polymerization of the butadiene monomer (forming the midblocks) resulting in one or more predetermined amount of 1,4 poly(butadiene) blocks followed by sequential polymerization of additional midblocks and hydrogenation to produce one or more crystalline midblocks of the final block copolymers.

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The crystalline block copolymers are made by sequential block copolymer synthesis, the percentage of crystallinity or $(-\text{CH}_2-)_{16}$ units should be at least about $(0.67)^4$ or about 20% and actual crystallinity of about 12%. For example, a selectively synthesized S-EBn-S copolymer having a ratio of 33:67 of 1,2 and 1,4 poly(butadiene) on hydrogenation will result in a midblock with a crystallinity of $(0.67)^4$ or 20%. For sake of simplicity, when n is a subscript of -EB-, n denotes the percentage of $(-\text{CH}_2-)_{16}$ units, eg, n = 33 or 20% crystallinity which is the percentage of $(0.67)^4$ or " $(-\text{CH}_2-)_{16}$ " units. Thus, when n = 28 or 72% of $(-\text{CH}_2-)_{16}$ units, the % crystallinity is $(0.72)^4$ or 26.87% crystallinity attributed to $(-\text{CH}_2-)_{16}$ units, denoted by -EB₂₈-. As a matter of convention, and for purposes of this specification involving hydrogenated polybutadiene: the notation -E- denotes at least about 85% of $(-\text{CH}_2-)_{16}$ units. The notation -B- denotes at least about 70% of $[-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-]$ units. The notation -EB- denotes between about 15 and 70% $[-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-]$ units. The notation -EBn- denotes n% $[-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-]$ units. For hydrogenated polyisoprene: The notation -EP- denotes about at least 90% $[-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-]$ units.

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midblock is substantially crystalline and flexibility low, physical blending with amorphous block copolymers such as S-EB-S, S-B-S, S-EP-S, S-EB-EP-S, (S-EP)_n and the like can produce more softer, less rigid, and more flexible crystal N-gel.

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Because of the (E) midblocks, the crystal N-gels of the invention exhibit different physical characteristics and improvements over substantially amorphous gels including damage tolerance, improved crack propagation resistance, improved tear resistance producing knotty tears as opposed to smooth tears, crystalline melting point of at least 28°C, improved resistance to fatigue, higher hysteresis, etc. Moreover, the crystal N-gels when stretched exhibit additional yielding as shown by necking caused by stress induced crystallinity. Additionally, the crystallization rates of the crystalline midblocks can be controlled and slowed depending on thermal history producing time delay recovery upon deformation.

Regarding resistance to fatigue, fatigue (as used herein) is the decay of mechanical properties after repeated application of stress and strain. Fatigue tests give information about

the ability of a material to resist the development of cracks or crazes resulting from a large number of deformation cycles. Fatigue test can be conducted by subjecting samples of amorphous and crystal N-gels to deformation cycles to failure (appearance of cracks, crazes, rips or tears in the gels).

Tensile strength can be determined by extending a selected gel sample to break as measured at 180° U bend around a 5.0 mm mandrel attached to a spring scale. Likewise, tear strength of a notched sample can be determined by propagating a tear as measured at 180° U bend around a 5.0 mm diameter mandrel attached to a spring scale.

Various block copolymers can be obtained which are amorphous, highly rubbery, and exhibiting minimum dynamic hysteresis:

Block copolymer S-EB-S

The monomer butadiene can be polymerized in a ether/hydrocarbon solvent to give a 50/50 ratio of 1,2 poly(butadiene)/1,4 poly(butadiene) and on hydrogenation no long runs of -CH₂- groups and negligible crystallinity, ie, about $(0.5)^4$ or 0.06 or 6% and actual crystallinity of about 3%. Due to the constraints of T_g and minimum hysteresis, conventional S-EB-S have ethylene-butylene ratios of about 60:40 with a crystallinity of about $(0.6)^4$ or 0.129 or 12% and actual crystallinity of about 7.7%.

Block copolymer S-EP-S

The monomer isoprene when polymerized will produce 95% 1,4 poly(isoprene)/5% 3,4 poly(isoprene) and upon hydrogenation will form amorphous, rubbery poly(ethylene-propylene) midblock and no long runs of -CH₂-- and no crystallinity.

Clean version of page 16, 5th and 6th paragraphs:

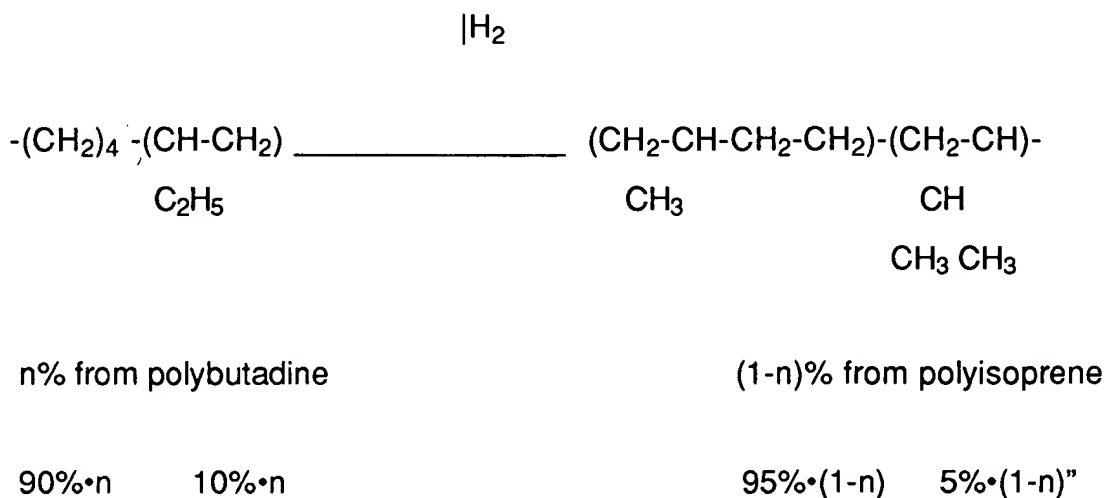
"The polymerization of a 20/80 mixture of isoprene/butadiene monomers in suitable ether/hydrocarbon solvents to give a 40:60 ratio of 1,2 and 1,4 poly(butadiene) will upon hydrogenation produce a low crystallinity of $(0.48)^4$ or 5.3%. The actual crystallinity would be approximately about 3.2%, which is negligible and results in a good rubbery midblock.

For purpose of convince and simplicity, the hydrogenated polybutadiene are denoted as

follows: -E- denotes at least 85% R-1 units, -B- denotes at least 70% R-2 units, -EB- denotes between 15 and 70% R-2 units, -EB_n- denotes n% R-2 units, and -EP- denotes 90% R-3 units.

Table I below gives the % of units on hydrogenation of polybutadiene/polyisoprene copolymer midblocks

B14
T, 540
CMT



Clean version of page 17:

where R-1 denotes $(-CH_2-)_4$,

R-2 denotes $-(CH-CH_2)-$,
 C_2H_5

R-3 denotes $-(CH_2-CH-CH_2-CH_2)-$, and
 CH_3

R-4 denotes $-(CH_2-CH)-$
 $CH_3 \ CH_3$

Therefore, the percentage that can crystallize is $[(-CH_2-)_4]_4$ since this is the chance of getting four $(-CH_2-)_4$ units in sequence. The percentage that will crystallize is about 60% of this.

BIS
crmt

n =	$(-CH_2-)_4$	$[(-CH_2-)_4]_4$	$0.6 \times [(-CH_2-)_4]_n$
0%	0%	0%	0%
20%	18%	0.1%	0.06%
40%	36%	1.7%	1.0%
60%	54%	8.5%	5.1%
80%	72%	26.9%	16.1%
100%	90%	65.6%	39.4%

This applies to polymerization in a hydrocarbon solvent. In an ether (eg, diethylether), the percentage units will be reduced so that crystallinity will be negligible.

T, 551

n =	$(-CH_2-)_4$	$[(-CH_2-)_4]_4$	$0.6 \times [(-CH_2-)_4]_n$
0%	0%	0%	0%
20%	5%	0.0006%	0.0004%
40%	10%	0.01%	0.006%
60%	15%	0.05%	0.03%
80%	20%	0.16%	0.10%
100%	25%	0.39%	0.23%

Clean version of page 19, 1st paragraph:

(four branches). Coupling with divinyl benzene give block copolymers which are very highly branched. Radial block copolymers suitable for use in forming the crystal N-gels of the present invention include: (S-E-EB-S)_n, (S-E-EP)_n, (S-B-EP)_n, (S-B-EB)_n, (S-E-EP-E)_n, (S-E-EB-B)_n, (S-B-EP-B)_n, (S-B-EB-B)_n, (S-E-B-EB)_n, (S-E-B-EP)_n, (S-EB-EP)_n, (S-E-EB-EP)_n, (S-E-EP-EB)_n, (S-B-EB-EP)_n, (S-B-EP-EB)_n, (S-E-EP-E-EP)_n, (S-E-EP-E-EB)_n, (S-EP-B-EP)_n, (S-B-EB-B-EB)_n, (S-B-EB-B-EP)_n, (S-E-EB-B-EP)_n, (S-E-EP-B-EB)_n, (S-E-EP-E-EP-E)_n, (S-B-EP-B-EP-B)_n, (S-E-EP-E-EB)_n, (S-E-EP-E-EP-EB)_n, (S-E-EP-E-EP-E)_n, (S-E-EP-EB-EP-EB-B)_n.

Clean version of page 20, 1st paragraph:

The crystal N-gels can be made in combination with or without a selected amount of one or more selected polymers and copolymers in amounts without substantially decreasing the desired properties. Such polymers includes: thermoplastic crystalline polyurethane elastomers with hydrocarbon blocks, homopolymers, copolymers, block copolymers, polyethylene, polypropylene, polystyrene, polyethylene copolymers, polypropylene copolymers, and the like. Other (vii) polymers and copolymers can be linear, star-shaped (radial), branched, or multiarm; these including: (SBS) styrene-butadiene- styrene block copolymers, (SIS) styrene-isoprene-styrene block copolymers, low and medium viscosity (S-EB-S) styrene-ethylene-butylene- styrene block copolymers, (S-EP) styrene-ethylene-propylene block copolymers, (S-EP-S) styrene-ethylene/propylene-styrene block copolymers, (S-E-EPS) styrene- ethylene-ethylene/propylene-styrene block copolymers, (SB)_n styrene-butadiene and (S-EB)_n, (S-EB-S)_n, (S-E-EP)_n, (SEP)_n, (SI)_n multi-arm, branched or star-shaped copolymers, polyethyleneoxide (EO), poly(dimethylphenylene oxide), teflon (TFE, PTFE, PEA, FEP, etc), optical clear amorphous copolymers based on 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) and tetrafluoroethylene (TFE), maleated S-EB-S block copolymer, polycarbonate, ethylene vinyl alcohol copolymer, and the like. Still, other polymers include homopolymers which can be utilized in minor amounts; these include: polystyrene, polydimethylsiloxane, polyolefins such as polybutylene, polyethylene, Hoechst Celanese/PEG 20000 UHMW polyethylene (Mw = 1,000,000-6,000,000), polyethylene copolymers, polypropylene, silicone (Tospearl 120A,

145A etc) and the like. Polyurethane thermoplastic crystalline copolymers with hydrocarbon midblocks based on saturated hydrocarbon diols (Handlin, D., Chin. S., and Masse. M., et al. "POLYURETHANE ELASTOMERS BASED ON NEW SATURATED HYDROCARBON DIOLS" Published Society of Plastics Industry, Polyurethane Division, Las Vegas, October 23, 1996) are also suitable for use in blending with the block copolymers (i-vi) used in forming the crystal N-gels of the invention. Such saturated hydrocarbon diols include hydroxyl terminated oligomers of poly(ethylene-butylene) (EB), poly(ethylene-propylene) (EP), -E-EB-, -E-EP-, -B-EP-, -B-EB-, -E-EP-E-, -E-EB-B-, -B-EP-B-, -B-EB-B-, -E-B-EB-, -E-B-EP-, -EB-EP-, -E-EB-EP-, -E-EP-EB-, -B-EB-EP-, -B-EP-EB-, -E-EP-E-EP-, -E-EP-E-EB-, -B-EP-B-EP-, -B-EB-B-EB-, -B-EB-B-EP-, -E-EB-B-EP-, -E-EP-B-EB-, -E-EP-E-EP-E-, -B-EP-B-EP-B-, -E-EP-E-EB-, -E-EP-E-EP-EB-, -E-EP-E-EP-E-, -E-EP-EB-EP-EB-B- and the like. As an example, thermoplastic polyurethane made with isocyanates and chain extenders such as TMPD and BEPD from saturated hydrocarbon diol KLP L-2203 having a hard segment contents of 22% exhibits clean phase separation of the hard and soft segments with glass a transition of -50°C. KLP L-2203 based TPU's can be mixed with the crystalline block copolymers to form soft crystal N-gels within the gel rigidity ranges of the invention.

Clean version of page 21, 3rd and 5th paragraphs:

Example of polymers, copolymers, and blends include: (a) Kraton G 1651, G 1654X; (b) Kraton G 4600; (c) Kraton G 4609; other suitable high viscosity polymer and oils include: (d) Tuftec H 1051; (e) Tuftec H 1041; (f) Tuftec H 1052; (g) Kuraray SEPS 4033; (h) Kuraray S-EB-S 8006; (i) Kuraray SEPS 2005; (j) Kuraray SEPS 2006, and (k) blends (polyblends) of (a)-(h) with other polymers and copolymers include: (1) S-EB-S/SBS; (2) S-EB-S/SIS; (3) S-EB-S/(SEP); (4) S-EB-S/(SEB)_n; (5) S-EB-S/(SEB)_n; (6) S-EB-S/(SEP)_n; (7) S-EB-S/(SI)_n; (8) S-EB-S/(SI) multiarm; (9) S-EB-S/(SEB)_n; (10) (SEB)_n star-shaped copolymer; (11) s made from blends of (a)-(k) with other homopolymers include: (12) S-EB-S/polystyrene; (13) S-EB-S/polybutylene; (14) S-EB-S/poly-ethylene; (14) S-EB-S/polypropylene; (16) SEP/S-EB-S, (17) SEP/SEPS, (18) SEP/SEPS/SEB, (19), SEPS/S-EB-S/SEP, (20), SEB/S-EB-S (21), EB-EP/S-EB-S (22), S-EB-S/EB (23), S-EB-S/EP (24), (25) (SEB)_n s, (26) (SEP)_n, (27) Kuraray 2007 (SEPS), (28) Kuraray 2002, (SEPS), (29) Kuraray 4055 (S-E-EP-S) (30)

Kuraray 4077 (S-E-EP-S) (31) Kuraray 4045 (S-E-EP-S) (32) (S-E-EP)_n, (33) (SEB)_n, (34) EPDM, (35) EPR, (36) EVA, (37) coPP, (38) EMA, (39) EEA, (40) DuPont Teflon AF amorphous fluoropolymers, (41) Dow polydimethylsiloxane, (42) maleated S-EB-S (maleation level 2-30%), (43) (EP)_n and the like.

Septon 4033 (SEEPS), 4045 (SEEPS), 4055 (SEEPS), and 4077 (SEEPS) are made from hydrogenated styrene isoprene/butadiene block copolymers, more specifically from hydrogenated styrene block polymer with 2-methyl-1,3-butadiene and 1,3-butadiene. Corresponding (SEP/EBS) copolymers can be made by proper control of polymerization.

B18
cm

Representative examples of commercial elastomers that can be combined with the block copolymers (i) described above include: Shell Kratons D1101, D1102, D1107, D1111, D1112, D1113X, D1114X, D1116, D1117, D1118X, D1122X, D1125X, D1133X, D1135X, D1184, D1188X, D1300X, D1320X, D4122, D4141, D4158, D4240, G1650, G1652, G1657, G1701X, G1702X, G1726X, G1750X, G1765X, FG1901X, FG1921X, D2103, D2109, D2122X, D3202, D3204, D3226, D5298, D5999X, D7340, G1650, G1651, G1652, G4609, G4600, G1654X, G2701, G2703, G2705, G1706, G2721X, G7155, G7430, G7450, G7523X, G7528X, G7680, G7705, G7702X, G7720, G7722X, G7820, G7821X, G7827, G7890X, G7940, FG1901X and FG1921X. Kuraray's SEP, SEPS, S-EB-S, S-EB-EP-S: Nos. 1001, 1050, 2027, 2003, 2006, 2007, 2008, 2023, 2043, 2063, 2050, 2103, 2104, 2105, 8004, 8006, 8007, H-VS-3 (S-V-EP)_n, Dexco polymers (Vector) having high styrene styrene ratios: 4411, 4461, 6241, DPX555, and the like. Septon 2104 has a high styrene content of 65 which is useful for blending with other copolymers to achieve the glassy phase criteria specified above.

The amorphous S-EB-S and (S-EB)_n copolymers can have a broad range of styrene to ethylene-

Clean version of page 22, 2nd and 3rd paragraphs:

B19

"The Brookfield Viscosity of a 5 weight percent solids solution in toluene at 30°C of 2006, 4045, 4055, 4077 typically range about 20-35, about 25-150, about 60-150, about 200-400 respectively. Typical Brookfield Viscosities of a 10 weight percent solids solution in toluene at 30°C of 1001, 1050, 2007, 2063, 2043, 4033, 2005, 2006, are about 70, 70, 17,

29, 32, 50, 1200, and 1220 respectively. Typical Brookfield Viscosity of a 25 weight percent solids solution in toluene at 25°C of Kraton D1101, D1116, D1184, D1300X, G1701X, G1702X are about 4000, 9000, 20000, 6000, 50000 and 50000 cps respectively. Typical Brookfield Viscosity of a 10 weight percent solids solution in toluene at 25°C of G1654X is about 370 cps. The Brookfield Viscosities of a 20 and 30 weight percent solids solution in toluene at 30°C of H-VS-3 are about 133 cps and 350 cps respectively.

B19
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Suitable block copolymers and their typical viscosities are further described. Shell Technical Bulletin SC:1393-92 gives solution viscosity as measured with a Brookfield model RVT viscometer at 25°C for Kraton G 1654X at 10% weight in toluene of approximately 400 cps and at 15% weight in toluene of approximately 5,600 cps. Shell publication SC:68-79 gives solution viscosity at 25°C for Kraton G 1651 at 20 weight percent in toluene of approximately 2,000 cps. When measured at 5 weight percent solution in toluene at 30°C, the solution viscosity of Kraton G 1651 is about 40. Examples of high viscosity S-EB-S triblock copolymers includes Kuraray's S-EB-S 8006 which exhibits a solution viscosity at 5 weight percent at 30°C of about 51 cps. Kuraray's 2006 SEPS polymer exhibits a viscosity at 20 weight percent solution in toluene at 30°C of about 78,000 cps, at 5 weight percent of about 27 cps, at 10 weight percent of about 1220 cps, and at 20 weight percent 78,000 cps. Kuraray SEPS 2005 polymer exhibits a viscosity at 5 weight percent solution in toluene at 30°C of about 28 cps, at 10 weight percent of about 1200 cps, and at 20 weight percent 76,000 cps. Other grades of S-EB-S, SEPS, (SEB)_n, (SEP)_n polymers can also be utilized in the present invention provided such polymers exhibits the required high viscosity. Such S-EB-S polymers include (high viscosity) Kraton G 1855X which has a Specific Gravity of 0.92, Brookfield Viscosity of a 25 weight percent solids solution in toluene at 25°C of about 40,000 cps or about 8,000 to about 20,000 cps at a 20 weight percent solids solution in toluene at 25°C."

Clean version of page 23, 4th paragraph:

b20

"Minor amounts of any compatible plasticizers can be utilized in forming the N-gels of the invention, but because of the non-tack property of the N-gels of the invention, the major amount of plasticizers used should be low viscosity plasticizers having viscosities

B²⁰
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advantageously of not greater than about 30 cSt @ 40°C, for example 30, 29, 28, 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, and the like. Such low viscosity plasticizers are commercially available as, for example, from Witco: Rudol, Ervol, Benol, Blandol, Carnation, Klearol, Semtol 100, Semtol 85, Semtol 70, Semtol 40; from Lyondell: Duroprime 55, 70, 90, Durprime DS L & M, Duropac 70, 90, Crystex 22, Crystex AF L & M, Tufflo 6006, 6016 and the like."

Clean version of page 24, 1st paragraph:

B²¹
L-14E (27-37 cst @ 100°F Viscosity), H-300E (635-690 cst @ 210°F Viscosity), Actipol E6 (365 Mn), E16 (973 Mn), E23 (1433 Mn), Kraton L-2203 and Kraton L-1203, EKP-206, EKP-207, HPVM-2203 and the like. Example of various commercially oils include: ARCO Prime (55, 70, 90, 200, 350, 400 and the like), Duraprim and Tufflo oils (6006, 6016, 6016M, 6026, 6036, 6056, 6206, etc) , other white mineral oils include: Bayol, Bernol, American, Blandol, Drakeol, Ervol, Gloria, Kaydol, Litetek, Lyondell (Duraprim 55, 70, 90, 200, 350, 400, etc), Marcol, Parol, Penetec, Primol, Protol, Sontex, Witco brand white oils including RR-654-P and the like. Generally, plasticizing oils with average molecular weights less than about 200 and greater than about 700 can also be used (e.g., H-300 (1290 Mn)).

Clean version of page 27, 2nd paragraph:

B²²
The crystal N-gels can also contain useful amounts of conventionally employed additives such as stabilizers, antioxidants, antiblocking agents, colorants, fragrances, flame retardants, flavors, other polymers in minor amounts and the like to an extent not affecting or substantially decreasing the desired properties. Additives useful in the crystal N-gel of the present invention include: tetrakis[methylene 3, -(3'5'-di-tertbutyl-4"-hydroxyphenyl) propionate] methane, octadecyl 3-(3",5"-di-tert-butyl-4"-hydroxyphenyl) propionate, distearyl-pentaerythritol-dipropionate, thiodiethylene bis-(3,5-ter-butyl-4-hydroxy) hydrocinnamate, (1,3,5-trimethyl-2,4,6-tris[3,5-di-tert-butyl-4-hydroxybenzyl] benzene), 4,4"-methylenebis(2,6-di-tert-butylphenol), stearic acid, oleic acid, stearamide, behenamide, oleamide, erucamide, N,N"-ethylenebisstearamide, N,N"-ethylenebisoleamide, steroyl erucamide, erucyl erucamide, oleyl palmitamide, stearyl stearamide, erucyl stearamide, calcium stearate, other

B22
CMT

metal sterates, waxes (e.g., polyethylene, polypropylene, microcrystalline, carnauba, paraffin, montan, candelilla, beeswax, ozokerite, ceresine, and the like), teflon (TFE, PTFE, PEA, FEP, etc), polysiloxane, etc. The crystal N-gel can also contain metallic pigments (aluminum and brass flakes), TiO_2 , mica, fluorescent dyes and pigments, phosphorescent pigments, aluminatetrihydrate, antimony oxide, iron oxides (Fe_3O_4 , $-\text{Fe}_2\text{O}_3$, etc.), iron cobalt oxides, chromium dioxide, iron, barium ferrite, strontium ferrite and other magnetic particle materials, molybdenum, silicones, silicone fluids, lake pigments, aluminates, ceramic pigments, ironblues, ultramarines, phthalocynines, azo pigments, carbon blacks, silicon dioxide, silica, clay, feldspar, glass microspheres, barium ferrite, wollastonite and the like. The report of the committee on Magnetic Materials, Publication NMAB-426, National Academy Press (1985) is incorporated herein by reference.

Clean version of page 28, 1st and 3rd paragraphs:

B23

The crystal N-gels denoted as "G" can be physically interlocked with a selected material denoted as "M" to form composites as denoted for simplicity by their combinations $G_n G_n$, $G_n G_n G_n$, $G_n M_n$, $G_n M_n G_n$, $M_n G_n M_n$, $M_n G_n G_n$, $G_n G_n M_n$, $M_n M_n M_n G_n$, $M_n M_n M_n G_n M_n$, $M_n G_n G_n M_n$, $G_n M_n G_n G_n$, $G_n M_n M_n G_n$, $G_n G_n M_n M_n$, $G_n G_n M_n G_n M_n$, $G_n M_n G_n G_n$, $G_n M_n G_n M_n M_n$, $M_n G_n M_n G_n M_n G_n$, $G_n G_n M_n M_n G$, $G_n G_n M_n G_n M_n G_n$ and the like or any of their permutations of one or more G_n with M_n and the like, wherein when n is a subscript of M , n is the same or different selected from the group consisting of paper, foam, plastic, fabric, metal, concrete, wood, glass, ceramics, synthetic resin, synthetic fibers or refractory materials and the like; wherein when n is a subscript of G , n denotes the same or a different gel rigidity of from about 2 gram to about 1,800 gram Bloom). The crystal N-gels of the composites are formed from copolymers, polymers, and plasticizers described above.

Sandwiches of crystal N-gel-material (i.e., crystal N-gel-material- crystal N-gel or material-crystal N-gel-material, etc.) are useful as dental floss, shock absorbers, acoustical isolators, vibration dampers, vibration isolators, and wrappers. For example the vibration isolators can be use under research microscopes, office equipment, tables, and the like to remove background vibrations. The tear resistance nature of the instant crystal N-gels are superior in performance to amorphous block copolymer gels which are much less resistance

to crack propagation caused by long term continue dynamic loadings.

B23
cont

The crystal N-gels are prepared by blending together the components including other additives as desired at about 23°C to about 100°C forming a paste like mixture and further heating said mixture uniformly to about 150°C to about 200°C until a homogeneous molten blend is obtained. Lower and higher temperatures can also be utilized depending on the viscosity of the oils and amounts of multiblock copolymers and polymer used. These components blend easily in the melt and a heated vessel equipped with a stirrer is all that is required. Small batches can be easily blended in a test tube using a glass stirring rod for mixing. While conventional large vessels with pressure and/or vacuum means can be utilized in forming large batches of the instant crystal N-gels in amounts of about 40 lbs or less to 10,000 lbs or more. For example, in a large vessel, inert gases can be employed for removing the composition from a closed vessel at the end of mixing and a partial vacuum can be applied to remove any entrapped bubbles. Stirring rates utilized for large batches can range from about less than 10 rpm to about 40 rpm or higher.

Clean version of page 29, 3rd paragraph:

B24

The crystal N-gels of the present invention exhibit one or more of the following properties. These are: (1) tensile strength of about 8×10^5 dyne/cm² to about 10^7 dyne/cm² and greater; (2) elongation of less than about 1,600% to about 3,000% and higher; (3) elasticity modules of about 10^4 dyne/cm² to about 10^6 dyne/cm² and greater; (4) shear modules of about 10^4 dyne/cm² to about 10^6 dyne/cm² and greater as measured with a 1, 2, and 3 kilogram load at 23°C; (5) gel rigidity of about less than about 2 gram Bloom to about 1,800 gram Bloom and higher as measured by the gram weight required to depress a gel a distance of 4 mm with a piston having a cross-sectional area of 1 square cm at 23°C; (6) tear propagation resistance greater than the tear resistance of amorphous S-EB-S gels at corresponding gel rigidities; (7) resistance to fatigue greater than the fatigue resistance of amorphous S-EB-S gels at corresponding gel rigidities; (8) and substantially 100% snap back recovery when extended at a crosshead separation speed of 25 cm/minute to 1,200% at 23°C. Properties (1), (2), (3), and (6) above are measured at a crosshead separation speed of 25 cm/minute at 23°C.

Clean version of page 30, 2nd paragraph:

B25 The weaved crystal N-gels are of great advantage for forming orthotics and prosthetic articles described above because such devices made from weaved crystal N-gels of fine to coarsed fabrics will allow for the human skin to breathe. The openings between weaved strands allows for air and oxygen transport between the skin and outer portions of the gel device body. Moreover, fine oriented or non-oriented crystal N-gels (made from SEEBs, SEEPS, E-S-E, SEEPES, SEPEEPS, SEB₄₅S and the like) in the form of threads or yarns can be produced by extruding, spinning or forced through a collection of jet nozzles to form a crystal N-gel spray to produce porous gel non-woven matting or webs which are skin oxygen/air breathe-able fabrics and articles. Unlike the elastomeric nonwoven webs made at 290°C of U.S. Patent 4,692,371, the crystal N-gels must be formed advantageously below 180°C, more advantageously at about 175°C or lower because of the extremely high amount of plasticizer components. If the crystal N-gels are heated to above 200°C and higher, the result is a puddle of hot liquid gel mass and not the porous individual form strands forming the desired fabrics. Furthermore, the crystal N-gels are superior in properties than any gels made from amorphous SEBS gels of substantially corresponding rigidities.

Clean version of page 32, 4th paragraph:

B26 In all cases, the tear strength of crystal N-gels are higher than that of amorphous gels. The rigidities of the crystal N-gels for use as dental floss advantageously should be selected to exhibit a propagating tear force (when propagating a tear as measured at 180° U bend around a 5.0 mm diameter mandrel attached to a spring scale) of at least about 1 Kg/cm, more advantageously at least 2 Kg/cm, and still more advantageously of about 3 Kg/cm and higher. For any gel to be considered useful for flossing, the gels should exhibit tear strengths of at least 2 Kg/cm and higher, advantageously of at least 4 Kg/cm and higher, more advantageously of at least 6 Kg/cm and higher, exceptionally more advantageously of at least 8 Kg/cm and higher. Typically, the tear propagation strength should range from about 5 Kg/cm to about 20 Kg/cm and higher, more typically from about less than 5 Kg/cm to about 25 Kg/cm and higher, especially more typically from about less than 6 Kg/cm to about 30 Kg/cm

B²⁶
cmT and higher, and exceptionally more typically from about less than 8 Kg/cm to about 35 Kg/cm and higher.

Clean version of pages 33-37, Examples II-XIV:

EXAMPLE II

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 200 white oil (plasticizer having Vis. cSt @ 40°C of 39.0) are melt blended, test and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and the gel tackiness are found to increase with increase amounts of plasticizers and the tack greater than 7.6 gram Tack.

EXAMPLE III

B²⁷ Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow S series poly(ethylene/styrene) random copolymer (250,000 Mw) having a high styrene content sufficient to form gel blends with total styrene content of 37 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Sementol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE IV

Gels of 100 parts of Septon 4045 (crystalline S-E/EP-S having a styrene content of 37.6) and 1,600, 1,200, 1,000, 800, 600, 500, 450, 300, 250 parts by weight of Duraprime Klearol white oil (plasticizer having Vis. CSt @ 40°C of 7-10) are melt blended, test and probe

samples molded, the bulk gel rigidities are found to be within the range of 2 to 2,000 gram Bloom and the tackiness is found to be less than about 1 gram Tack.

EXAMPLE V

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of Septon 2104 (Amorphous SEPS having a high styrene content of 65) and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Sementol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE VI

B27
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Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow M series poly(ethylene/styrene) random copolymer (350,000 Mw) having a high styrene content sufficient to form gel blends with total styrene content of 37 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Sementol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE VII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow E series poly(ethylene/styrene) random copolymer (240,000 Mw) having a high styrene content sufficient to form gel blends with total

65

styrene content of 37 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Sementol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE VIII

B27
C-1
Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with polystyrene homopolymers (having Mw of 3,000; 4,000; 5,000; 6,000; 7,000; 8,000; 9,000; 10,000; 11,000; 12,000; 13,000; 14,000; 15,000; 16,000; 17,000; 18,000; 19,000; 20,000; 30,000; 40,000; 50,000; 60,000; 70,000; 80,000; 90,000) in sufficient amounts to form gel blends with total styrene content of 37, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Sementol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 2,000 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE IX

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow M series poly(ethylene/styrene) random copolymer (350,000 Mw) having a high styrene content sufficient to form gel blends with total styrene contents of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Sementol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram

66

to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE X

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CMI

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow S series poly(ethylene/styrene) random copolymers (with Mw of 140,000; 250,000 and 340,000) having a high styrene content sufficient to form gel blends with total styrene content of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XI

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow E series poly(ethylene/styrene) random copolymers (with Mw of 250,000; 340,000 and 400,000) having a high styrene content sufficient to form gel blends with total styrene content of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XII

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with sufficient amounts of a Dow M series poly(ethylene/styrene) random copolymer (with Mw of 250,000; 340,000 and 400,000) having a high styrene content sufficient to form gel blends with total styrene content of 40, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XIII

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CMT

Gels of 100 parts of Dow E series crystalline poly(ethylene/styrene) random copolymer (with Mw of 250,000; 340,000 and 400,000) having a high styrene content sufficient to form gel blends with total styrene content of 37, 40, 45, 48, 50, 55, and 60 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 1,800 gram Bloom and the notched tear strength and resistance to fatigue of the gel at corresponding rigidities are found to be greater than that of amorphous gels of Example I, while tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XIV

Gels of 100 parts of Septon crystalline (SEEPS) copolymers 4033, 4055, and 4077 in combination with polystyrene (of 2,500 Mw, 4,000 Mw, 13,000 Mw, 20,000 Mw, 35,000 Mw, 50,000 Mw, and 90,000 Mw; poly(alpha-methylstyrene) (of 1,300 Mw, 4,000 Mw; poly(4-

methystyrene)(of 72,000 Mw), Endex 155, 160, Kristalex 120, and 140) in sufficient amounts to form gel blends with total styrene content of 37, 45, 48, 50, and 55 by weight of copolymers and 800, 600, 500, 450, 300, 250 parts by weight of Duraprime 55, 70, Klearol, Carnation, Blandol, Benol, Semtol 85, 70, and 40 (plasticizers having Vis. CSt @ 40°C of less than 20) are melt blended, tests, and tack probe samples molded, the bulk gel rigidities are found to be within the range of 2 gram to 2,000 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XV

Examples XIV is repeated and gels of 100 parts of (S-EB₄₅-EP-S), (S-E-EB₂₅-S), (S-EP-E-EP-S), (S-E-EB-S), (S-E-EP-S), (S-E-EP-E-S), (S-E-EP-EB-S), (S-E-EP-E-EP-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-E-S), (S-E-EP-E-EB-S), (S-E-EP-E-EP-EB-S), and (S-E-EP-E-EP-E-S) block copolymers are each melt blended, tests and probe samples molded, the bulk gel rigidities are found to be within the range of 2 to 1,800 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XVI

Example XIV is repeated and minor amounts of 2, 5, 10 and 15 parts of the following polymers are formulated with each of the triblock copolymers: styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, low viscosity styrene-ethylene-butylene-styrene block copolymers, styrene-ethylene-propylene block copolymers, styrene-ethylene-propylene-styrene block copolymers, styrene-butadiene, styrene-isoprene, polyethyleneoxide, poly(dimethylphenylene oxide), polystyrene, polybutylene, polyethylene, polypropylene, high ethylene content EPDM, amorphous copolymers based on 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluoroethylene. The bulk gel rigidities of each of the formulations are found to be within the range of 2 gram to 2,000 gram Bloom and tack is found to decrease with decreasing plasticizer content and in all instances substantially lower than the gels of Example I and II.

EXAMPLE XVII

*B²⁷
cr*

Molten gels of Examples III-XVI are formed into composites with paper, foam, plastic, elastomers, fabric, metal, concrete, wood, glass, ceramics, synthetic resin, synthetic fibers, and refractory materials and the resistance to fatigue of the composite-crystal N-gels at corresponding rigidities are found to be greater than that of the composite-amorphous gels of Example I.
